



Thermally Stable Piezoelectric and Pyroelectric Polymers

Neither mechanical nor solvent treatment is necessary for orientation of polymer molecules.

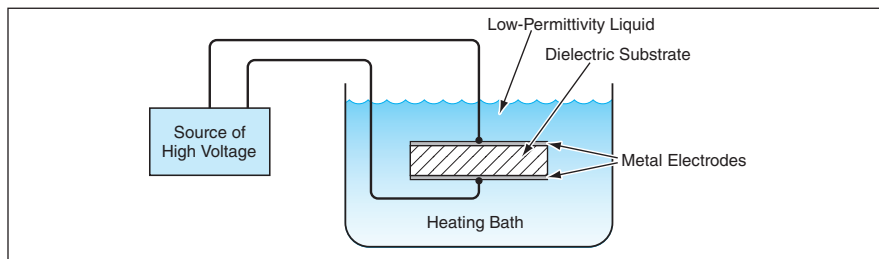
Langley Research Center, Hampton, Virginia

A class of thermally stable piezoelectric and pyroelectric polymers, and an improved method of making them, have been invented. These polymers can be used as substrates for a wide variety of electromechanical transducers, sensors, and actuators.

In order to enable a material to produce an electrostatic potential in response to mechanical excitation (piezoelectricity) or in response to thermal excitation (pyroelectricity), the material must be electrically polarized; that is, its molecules must be at least partially aligned in a preferred electric-dipole orientation. The preferred orientation or polarization occurs naturally in quartz and some crystalline materials, and can be induced in some ceramics and polymers by application of strong electric or mechanical fields.

Prior to this invention, poly(vinylidene fluoride) [PVF₂] was the only commercially available piezoelectric polymer. In order to be able to exploit the piezoelectricity of PVF₂, it was necessary to orient its molecules by mechanical drawing of sheets or by dissolving the PVF₂ in a solvent and then subjecting it to an electric field while causing the solvent to evaporate. In contrast, the polymers of the present invention are rendered piezoelectric and/or pyroelectric by means of an orientation process that does not involve either a solvent or a mechanical treatment.

The polymers suitable for this invention include polyarylates, polyquinoxalines, polyphenylene ethers, polycarbonates, polyphenylene sulfides, polysulfones, polyaryletherketones, polyimides, polyarylene ethers, polybenzimidazoles,



A Polymer Substrate Is Heated to its softening temperature in a low-permittivity dielectric liquid while a high voltage is applied to metal electrodes on opposite faces to induce electric polarization. When the electrode/substrate/electrode sandwich is cooled, the polarization remains frozen into the substrate.

polyazomethines and possibly other thermally stable polymers. These polymers have softening temperatures greater than about 100 °C, and, once polarized, they retain their polarizations (and, hence, their piezoelectric and pyroelectric properties) at temperatures up to their softening temperatures.

A polymeric substrate to be rendered piezoelectric and/or pyroelectric according to the invention is prepared by depositing metal electrodes on opposite faces. The electrode metal can be gold, silver, or any other suitable low-electrical-resistivity metal that is not readily oxidized at the temperature to be used in the treatment described next. The metal electrodes are connected to a source of high voltage, and the electrode/substrate/electrode sandwich is immersed in a heating bath containing silicone oil or other suitable low-permittivity dielectric liquid (see figure). In the bath, the electrode/substrate/electrode sandwich is heated to the softening temperature of the polymer to increase the mobility of the polymer molecules. A voltage is

applied to the electrodes to generate an electric field (typically between 50 and 200 MV/m) large enough to orient the polymer molecules but not so large as to cause dielectric breakdown of the polymer substrate. The voltage can be low-frequency AC or DC. The voltage is maintained for an interval of time sufficient to obtain the desired degree of polarization. The electrode/substrate/electrode sandwich is then cooled while maintaining the voltage. Once the temperature is well below the softening temperature, the voltage is turned off, and the induced orientation remains frozen into the polymer.

This work was done by Joycelyn O. Simpson and Terry L. St. Clair of Langley Research Center. Further information is contained in a TSP (see page 1).

This invention has been patented by NASA (U.S. Patent Nos. 5,891,581, 5,909,905, and 6,379,809). Inquiries concerning nonexclusive or exclusive license for its commercial development should be addressed to the Patent Counsel, Langley Research Center, at (757) 864-3521. Refer to LAR-15279.

Combustion Synthesis of Ca₃(PO₄)₂ Net-Shape Surgical Implants

More-biocompatible materials are produced in fewer processing steps.

John H. Glenn Research Center, Cleveland, Ohio

Self-propagating high-temperature combustion synthesis (SHS) is the basis of a method of making components of porous tricalcium phosphate [Ca₃(PO₄)₂] and related compounds in net sizes and

shapes for use as surgical implants that are compatible with bone. Ca₃(PO₄)₂-based materials are among those preferred for use in orthopedic, restorative, and reconstructive surgery. As explained

below, the SHS method offers advantages over prior methods of manufacturing Ca₃(PO₄)₂-based surgical implants.

Ca₃(PO₄)₂ occurs in at least two crystalline forms: a monoclinic form de-

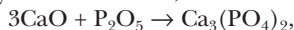
noted the α phase and an orthorhombic form denoted the β phase. The β phase is the preferred form for bone replacements because it can be resorbed by the body, facilitating bone remodeling. At an appropriate porosity, β $\text{Ca}_3(\text{PO}_4)_2$ resembles natural bone and serves as a scaffold into which osteogenic cells can migrate. Thus, bone becomes directly attached to and grows into a β $\text{Ca}_3(\text{PO}_4)_2$ implant. The body generally resorbs β $\text{Ca}_3(\text{PO}_4)_2$ within about two years, replacing it with natural bone.

Prior methods of making surgical implants of $\text{Ca}_3(\text{PO}_4)_2$ and related materials have not yet been perfected. The prior methods involve, variously, synthesis of $\text{Ca}_3(\text{PO}_4)_2$ -containing bioceramics from aqueous solutions, sintering, sol-gel processing, and/or casting of polymeric foams mixed with slurries of $\text{Ca}_3(\text{PO}_4)_2$ -containing bioceramic particles. All of these prior methods are energy- and labor-intensive, and each requires several time-consuming steps. Of particular interest is the sintering method, which includes molding by compacting a powder into a die having the size and shape of the desired part, then heating to temperature just high enough that the powder particles undergo solid-state bonding to each other but do not melt. The great disadvantage of this method is that at the high sintering temperature, β $\text{Ca}_3(\text{PO}_4)_2$ becomes converted to α $\text{Ca}_3(\text{PO}_4)_2$, which is not preferable as a bone replacement material.

Relative to any of the prior methods, the present SHS-based method requires

fewer steps, takes less time, enables better tailoring of porosity, and yields a greater ratio between the desired β phase and the undesired α phase. Processing according to this method begins with preparation of a mixture of CaO and P_2O_5 powders and possibly other ingredients described below. Processing must be done in a protective dry, nonreactive atmosphere (e.g., argon) because P_2O_5 is hygroscopic and strongly reactive. The mixture is compacted into a combustible or noncombustible die having the size and shape of the desired part. If the die is noncombustible, the preform of compacted powder is then removed from the die carefully so as not to deform or break it.

Next, the compacted powder preform is heated to initiate the main combustion synthesis reaction,



which is accompanied by some other reactions that yield a variety of calcium-, oxygen-, and phosphorus-containing byproducts. The main combustion synthesis reaction is exothermic and self-sustaining: once it has been initiated, a wavefront comprising a reaction zone moves through the mixture. In the reaction zone and its vicinity, the reactant having the lowest melting temperature momentarily spreads by means of capillary action, leading to a large dispersion of the reaction products.

In general, $\text{Ca}_3(\text{PO}_4)_2$ is formed if the mixture contains between about 60 and 90 mole percent of CaO and between about 10 and 40 mole percent of P_2O_5 .

The proportions of these ingredients can be adjusted to tailor the proportions of the α and β phases of $\text{Ca}_3(\text{PO}_4)_2$ in the combustion-synthesis product. Optionally, the reaction mixture can include one or more dopants and/or a gasifying agent. Also optionally, the combustion-synthesis product can be subjected to a further process of controlled heating and cooling to increase the ratio between the β and α phases of $\text{Ca}_3(\text{PO}_4)_2$.

Process parameters can also be varied to tailor the degree of porosity, the proportion of interconnected pores, and the shapes of the pores in the finished product, and to impart functionally graded porosity as might be required for a particular application. Examples of such parameters include, but are not limited to, the pressure used to compact the reactant mixture, the amount of the gasifying agent, the proportions of CaO and P_2O_5 in the reactant mixture, the sizes of the reactant powder particles, and the pressure of the atmosphere in which the reaction takes place.

This work was done by Reed A. Ayers, Martin Castillo, Guglielmo Gottoli, John J. Moore, and Steven J. Simske of the Colorado School of Mines for Glenn Research Center. Further information is contained in a TSP (see page 1).

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17951-1.